Chelate Chemistry. I. Tropolone and Aminotroponimine Derivatives of the Main-Group Elements

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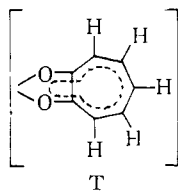The tropolone and N,N'-dimethylaminotroponimine chelate chemistry of the main-row elements of groups III, IV, and V has been explored. Especially noteworthy of the chelates prepared are the cationic derivatives of boron, silicon, germanium, tin, and phosphorus. The boron derivative of N,N'-dimethylaminotroponimine, $B(C_9H_{11}N_2)_2^+$, resists attack of strong aqueous acid and base, whereas the other metal derivatives of this amine are subject to acid-catalyzed hydrolysis. All of the tropolone chelates are rapidly hydrolyzed by aqueous sodium hydroxide. With tropolone, eight-coordinate species were obtained from indium, lead, and tin.

Introduction

The facility with which a given atom can achieve a high coordination number has not been well characterized for molecular species. It was once assumed that first-row elements could not surpass a coordination number of four yet now there are many examples of five and six coordination, notably for boron, e.g., elemental boron[1] and B_5H_9.[2] Recently examples of eight coordination for third-row elements have been reported as in the diarsine chelate of titanium(IV)[3] and ten coordination has been described for a chelate hydrate of a rare earth ion.[4] To exploit high-coordination chemistry, it is apparent from the existing literature that the more favorable ligands are (A) small atoms such as fluorine[3b,5] or hydrogen[6]; (B) other metal atoms as in $Mo_6Cl_{14}^{2-}$, $Ta_6Cl_{12}^{2+}$, and the polyhedral boranes; and (C) multidentate ligands.[4] Ligands of type B are ideally suited to the lighter elements where the number of energetically available orbitals are severely limited and multicenter bond formation is the only path to very high coordination numbers. We are pursuing the question of maximum coordination for elements with all these types of ligands, and in this paper the preliminary results on chelate studies are described.

The multidentate ligand has much to recommend it as a probe of high-coordination chemistry although in many instances steric factors preclude high coordination numbers in such complexes. One bidentate ligand that is quite compact by virtue of the coplanar ring structure is T which is derived from tropolone.

T

Considerable stability should be conferred to chelates based on this ligand because of the delocalized π-system.[7] Related to the tropolone ligand T is A which

A

is derived from N,N'-dimethylaminotroponimine. This ligand is capable of extensive π-electron delocalization in chelate structures as documented in studies of the amine[8a] and of boron[8b] and transition metal derivatives.[8c] Steric effects resulting from intramolecular R(N)-R(N) repulsion have been clearly in evidence for bischelates based on A.[8c] Thus, ligand A can serve as a monitor to T for systems in which steric crowding becomes significant.

Results and Discussion

Group III Elements.—Boron tribromide and tropolone react in nonaqueous media to give nearly quantitative yields of the bromide salt of the tetrahedral T_2B^+ cation. This cation can also be prepared from boric acid and tropolone in acidic aqueous solution. With N,N'-dimethylaminotroponimine and boron tribromide, the analogous A_2B^+ cation is generated. Unlike the tropolone chelate, this amino cation cannot be formed in aqueous media; thermodynamically, it is unstable toward hydrolysis. Holmquist and Benson[8b] have prepared monoaminotroponiminates of boron, e.g., ABX_2 and ABR_2.

Trihalides of the heavier elements of group III, i.e., aluminum through thallium, and the rare earths (as well as those of the transition elements) are converted by tropolone to the octahedral MT_3 chelates. The aluminum and indium compounds have been previously reported.[7] Solubility of these chelates is relatively low even in polar solvents; however, the gallium derivative proved sufficiently tractable to establish its monomeric behavior in chloroform. All of the MT_3 chelates are readily degraded by aqueous base, but are unaffected by acids. They, in fact, were prepared in acidic aqueous solution. On the basis of X-ray powder pattern comparison, there appear

(1) J. L. Hoard, R. E. Hughes, and R. E. Sands, *J. Am. Chem. Soc.*, **80**, 4507 (1958); L. V. McCarty, J. S. Kasper, F. H. Horn, B. F. Decker, and A. E. Newkirk, *ibid.*, **80**, 2592 (1958).

(2) W. J. Dulmage and W. N. Lipscomb, *Acta Cryst.*, **5**, 260 (1952).
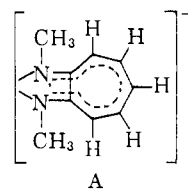
(3) (a) R. J. H. Clark, J. Lewis, R. S. Nyholm, P. Pauling, and G. B. Robertson, *Nature*, **192**, 222 (1961); (b) R. J. H. Clark, D. L. Kepert, and R. S. Nyholm, *ibid.*, **199**, 559 (1963).

(4) X-Ray analysis showed the tetrahydrate of the ethylenediaminetetraacetic acid derivative of La(III) to be ten-coordinate: J. L. Hoard, Fourth Rare Earth Research Conference, Session III, Phoenix, Ariz., April 22–25, 1964.

(5) Coordination numbers of seven and eight are fairly common in complex fluoro anions, at least for the solid state: J. L. Hoard, *J. Am. Chem. Soc.*, **61**, 1252 (1939); E. L. Muetterties, *ibid.*, **79**, 1004 (1957); and K. J. Packer and E. L. Muetterties, *ibid.*, **85**, 3035 (1963).

(6) ReH_9^{2-} is the best example for hydrogen as a ligand in a high-coordinate species: K. Knox and A. P. Ginsberg, *Inorg. Chem.*, **3**, 555 (1964).

(7) Tropolone chelates of a number of metals have been described: *cf.* B. E. Bryant, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 3784 (1953).

(8) (a) R. E. Benson, *ibid.*, **82**, 5948 (1960); (b) H. E. Holmquist and R. E. Benson, *ibid.*, **84**, 4720 (1962); (c) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *ibid.*, **85**, 397 (1963).

to be three characteristic lattices for MT_3 chelates. The aluminum, gallium, and chromium derivatives belong to one class, europium and lanthanum to the second, and indium, thallium, and iron to the third.

Indium trichloride and sodium tropolonate yield the eight-coordinate salt, $Na^+InT_4^-$. Under similar conditions, gallium trihalides form only the octahedral GaT_3. Formation of an anionic chelate is less favorable than for a neutral or cationic species; and thus, tropolone does not provide a good diagnostic test for eight coordination for gallium.

Group IV.—The tetrahalides of silicon, germanium, and tin react with N,N'-dimethylaminotroponimine, or preferably its lithium salt, to give octahedral A_3M^+ chelates. These cationic chelates are thermodynamically unstable towards hydrolysis and cannot be prepared in aqueous media.

Tropolone and silicon tetrachloride give T_3Si^+ as the sole chelated product as do silicic acid and tropolone in acidic aqueous solution. The same type of cationic chelate is produced from tropolone and germanium tetrachloride in aqueous medium. In nonaqueous media, germanium tetrachloride tends to give a material of the composition T_2GeCl_2 which undergoes reaction with water to give T_3Ge^+. Under forcing conditions, the simple chloride salt $T_3Ge^+Cl^-$ is formed in nonaqueous media. The only tin chelates generated from tin tetrahalides and tropolone in either aqueous or nonaqueous media have the composition T_2SnX_2.

Single crystal X-ray analysis of T_2SnCl_2 established that the unit cell contains eight T_2SnCl_2 units thus rigorously excluding the ionic formulation $(T_3Sn^+)_2$-$SnCl_6^{-2}$. Presumably, T_2SnCl_2 is a simple octahedral species.[9] In solution, T_2SnCl_2 gives no evidence of ionization to a T_3Sn^+ cation. The germanium analog, T_2GeCl_2, is isomorphous with T_2SnCl_2.

A tristropolone derivative of tin, T_3SnCl, was obtained from sodium tropolonate and tin tetrachloride. Unlike the analogous silicon and germanium compositions, this tin chelate gave no evidence of electrolyte behavior. It is relatively insoluble in polar solvents and does not undergo metathetical reactions that are so characteristic of the T_3M^+ and A_3M^+ salts. Furthermore, antimony pentachloride abstracts tropolone rather than chloride ion from T_3SnCl. A similar ex-

$$T_3SnCl + SbCl_5 \longrightarrow T_2SnCl_2 + TSbCl_4$$
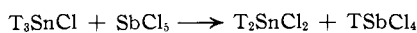
change occurs with $FeCl_3$. In contrast, $T_3Si^+Cl^-$ yields $T_3Si^+SbCl_6^-$ and $T_3Si^+FeCl_4^-$ with $SbCl_5$ and $FeCl_3$, respectively. The chloride, T_3SnCl, sublimes at $\sim 290°$ $(0.01~\mu)$; therefore, it must be monomolecular in the gaseous state. Thus, T_3SnCl appears to be better visualized as a seven-coordinate[10] structure than as a salt. This behavior of T_3SnCl contrasts sharply with that of A_3SnCl which is a strong electrolyte. Failure of A_3Sn^+ to securely bind a halide ion must be ascribed to the more effective steric screening of tin by the N-CH_3 groups.

Phenyltin trichloride and tropolone yield C_6H_5Sn-ClT_2,[11] which is converted to $C_6H_5SnT_3$ by reaction with the sodium salt of tropolone. The molecular weight of $C_6H_5SnT_3$ in dichloromethane is that of a monomer. These data are suggestive of a seven-coordinate structure.

Lead tetraacetate and tropolone give directly the eight-coordinate PbT_4. A similar chelate is obtained with tin from sodium tropolonate and tin tetrahalides or T_2SnCl_2. The infrared spectra of PbT_4 and SnT_4 are similar to those of CeT_4 and ZrT_4.[12] Thus, eight coordination can at the very least be achieved with tropolone and a fourth-row element as was observed in group III.

Reaction of $T_3Ge^+Cl^-$ and silver tropolonate in aqueous acetonitrile gives a pale orange solid of the composition $GeT_4\cdot 2H_2O$. The proton n.m.r. spectrum of $GeT_4\cdot 2H_2O$ shows two kinds of aromatic CH resonance, one multiplet characteristic of the chelate and one characteristic of the tropolone anion. Thus, this orange solid must simply be the tropolone salt of the chelate cation GeT_3^+. The analogous silicon compound $SiT_4\cdot 2H_2O$ is chemically similar to and isomorphous with $GeT_4\cdot 2H_2O$. In vacuo, $GeT_4\cdot 2H_2O$ and $SiT_4\cdot 2H_2O$ dehydrate to black microcrystals of GeT_4 and SiT_4, respectively. These black crystals hydrate rapidly on exposure to the atmosphere to regenerate the dihydrates. All available spectroscopic data (infrared and n.m.r.) suggest that these black chelates are primarily salts, i.e., $MT_3^+T^-$.[13]

Group V.—Tropolone and phosphorus pentachloride spontaneously yield the chloride salt of T_3P^{2+}. This is the least stable of the tropolone chelate cations. Hydrolysis in water is moderately fast and is irreversible, unlike that for T_2B^+, T_3Si^+, and T_3Ge^+. No cationic tropolone derivative of phosphorus could be isolated from phosphoric acid and tropolone in aqueous media. In contrast, arsenic(V) oxide does react with tropolone in acidic aqueous solution to yield halide salts of the $T_2As(OH)_2^+$ cation. This arsenic cation undergoes metatheses in acidic media, but in water it is largely degraded to T^- and some chelate arsenic compound, probably $TAsO(OH)_2$, as evidenced by proton n.m.r. spectra.

Addition of antimony pentachloride to a nonaqueous solution of tropolone results in precipitation of the salt $T_2H^+SbCl_6^-$. Remaining in solution is the simple octahedral derivative $TSbCl_4$ which can be obtained as a yellow crystalline solid from the solution. The group V trichlorides react with tropolone but give no cationic chelates. With antimony and bismuth, the products have the composition T_2MCl. These are monomeric, and there was no evidence that T_2M^+ species might be present in that solubility in polar solvents proved quite low, and attempts to effect metatheses were unsuccessful. Reaction of $SbCl_5$ with T_2SbCl gave $TSbCl_4$; exchange of tropolone anion rather than Cl^- occurred. These chelates are apparently pseudo-octahedral structures, $:MT_2Cl$.

Cationic Chelates from Tropolone.—The tropolone chelate cations T_2B^+, T_3Si^+, and T_3Ge^+ show the

(9) T_2SnX_2 could have a seven- or even eight-coordinate tin atom through X–Sn–X bridge bonds. Spectrally T_2SnCl_2 is identical with T_2TiCl_2 which is the only chelate produced from tropolone and $TiCl_4$, but T_2SnCl_2 and T_2TiCl_2 are not isomorphous by X-ray analysis.

(10) T_3SnCl could be eight coordinate in the solid state through bridging chlorine atoms.

(11) The same product is obtained from either diphenyltin dichloride or triphenyltin chloride.

(12) The X-ray powder patterns of the tin and lead compounds are similar. There are no similarities between the powder patterns of SnT_4, CeT_4, and ZrT_4. ZrT_4 and HfT_4 are isomorphous, and CeT_4 and ThT_4 are isomorphous. The zirconium, hafnium, and thorium compounds sublime at $\sim 300°$ $(0.01~\mu)$, but CeT_4 and PbT_4 decompose before any volatilization occurs.

(13) Characterization of suspected eight-coordinate metal chelates derived from tropolone will be detailed in another paper.

general properties of large cations. Their salts are strong electrolytes as evidenced by conductivity studies. The chloride salts readily undergo metatheses with salts of large anions, e.g., I^-, PF_6^-, and $B_{10}Cl_{10}^{-2}$, to yield relatively water-insoluble salts. Reduction in aqueous media is not a facile process as evidenced by polarographic studies. Borohydride ion reduction of T_2B^+ does, however, yield a neutral species of the composition T_2B^0. This reduction product is, however, not paramagnetic and apparently results from hydride ion addition to one of the tropolone rings to give $(C_7H_6O_2)B(O_2C_7H_5)$. All of the cationic chelates described above are subject to degradation by hydroxyl ion. Hydrolysis is complete at a pH of 8 or greater as demonstrated analytically and spectrophotometrically. For the boron, silicon, and germanium chelates, the hydrolysis is reversible on addition of acid. No evidence of reversibility was found in the hydrolysis of T_3P^{2+}.

Hydrolysis of the tris(acetylacetonato)silicon cation, $Si(O_2C_5H_7)_3^+$, which is formally analogous to the tropolone chelates, has been characterized as kinetically first order in chelate and in base.[14] It was concluded that this hydrolysis is the first clear-cut example of an S_N2 reaction for an octahedral species and that the activated complex must comprise a seven-coordinate silicon entity.[14] Seven coordination for silicon, even in a reaction intermediate or activated complex, is a point important to this study; and accordingly, this question was pursued for the tropolone cation chelates. We followed the basic hydrolysis of a variety of tropolone metal chelates in a medium enriched in O^{18}.[15] Enrichment of tropolone in O^{18} occurs in the hydrolysis of all the cationic derivatives, T_2B^+, T_2Si^+, T_3Ge^+, and T_3P^{2+}, but not of the neutral chelates such as T_3Al. Furthermore the silicon chelate cation derived from dibenzoylmethane hydrolyses in O^{18}-enriched aqueous base with enrichment of the dibenzoylmethane. Thus, attack of these cation chelates by hydroxyl ion does not initiate at the central element but at a carbon atom adjacent to the chelate oxygen atom. Molecular models (Fig. 1) show that there is no steric blocking of the central element or the carbon atoms in all these tropolone chelates.

Acidic solutions of T_2B^+ and of T_3Ge^+ with tropolone show no evidence of fast ligand exchange up to 140° by n.m.r. criterion. Within this range there is clear evidence of hydrolysis. For a solution of T_3Si^+ and tropolone, there is merging of the chelate and the tropolone CH multiplet resonances at ~140°. The lifetime of the ligand as anion or as chelate is of the order of magnitude of a millisecond at 140°.

Cationic Chelates from N,N'-Dimethylaminotroponimine.—The clean generation of the octahedral chelates A_3M^+ from the group IV tetrahalides, silicon through tin, contrasts with the tropolone behavior. The relative reluctance of ligand A to form higher coordination number derivatives is ascribed to an intramolecular repulsion of $N-CH_3$ groups which is clearly shown in molecular models (Fig. 2). All of these amine chelates are stable to aqueous strong base as might be expected from the effective shielding

of the central element by the ligands, again in contrast to the tropolone chelates. Moreover, nucleophilic attack at the carbon atom directly attached to nitrogen is apparently not a low-energy process. Aqueous acid does, however, rapidly degrade these octahedral chelates and the hydrolysis is irreversible. Acid hydrolysis most probably proceeds by proton attack at the nitrogen atoms of the chelate. Basicity of these nitrogen atoms was clearly shown by the absorption of hydrogen chloride by the chelate salts to give MCl_4 and AH^+Cl^-. By comparison, $T_3Si^+PF_6^-$ does not absorb hydrogen chloride at 25°, thus the strongly basic character of N,N'-dimethylaminotroponimine, as compared to the relatively acidic tropolone, prevails even in the chelate derivatives.

The salts of the boron derivative of N,N'-dimethylaminotroponimine, $A_2B^+X^-$, function as strong electrolytes as evidenced by conductance studies, and the base, $A_2B^+OH^-$, prepared by the ion-exchange method, exhibited in titration studies the behavior of a strong base. In these properties, the boron cation resembles the group IV cations, A_3M^+. The similarity ends where acid is concerned. The salt $A_2B^+PF_6^-$ does not detectably absorb hydrogen chloride from -78 to 25°, and the cation suffers no degradation in dilute acids, e.g., 20% sulfuric acid at 100°. Figure 3 shows that in A_2B^+ the nitrogen atoms are not significantly protected by steric crowding. Thus, it would appear that the donor activity of the ligand nitrogen atoms has been absorbed by some mechanism into the A_2B^+ system to a far greater extent than in the group IV A_3M^+ species. This boron cation can be degraded by acid, but it requires exposure to ~30% hydrochloric acid at 70° for several days.

The aminotroponimine chelates show greater resistance to reduction than do the tropolone chelates. This behavior was appraised from polarographic studies (no clean, reversible, one-electron reduction observed) and chemical studies. Borohydride ion and A_2B^+ simply precipitate the $A_2B^+BH_4^-$ salt, whereas T_2B^+ is converted to HTBT as noted above. Lithium aluminum hydride and A_2B^+ gave a monomeric material which analyzed for A_2B but was diamagnetic. Spectroscopic data indicated that hydride addition to one of the chelate ligands had occurred to form $C_9H_{11}N_2BN_2C_9H_{12}$.

Experimental

$T_2B^+Br^-$.—A solution of boron tribromide (5.0 g., 0.02 mole) in 25 ml. of chloroform was added to tropolone (4.9 g., 0.04 mole) dissolved in 120 ml. of chloroform. An oil separated during the addition. After the addition, a rapid stream of nitrogen was passed through the mixture at reflux for 2 hr. to remove the hydrogen bromide. Evaporation of the chloroform under reduced pressure left a yellow solid, which was recrystallized from water containing a small amount of sodium bromide. Yellow crystals of $T_2B^+Br^-$ were obtained in 95% yield.

$T_3Si^+Cl^-$.—In an analogous procedure, silicon tetrachloride (6.9 g., 0.04 mole) in 50 ml. of chloroform was added to tropolone (14.9 g., 0.12 mole) in 200 ml. of chloroform. A white solid separated which was isolated by filtration and recrystallized from water. The chelate, $T_3Si^+Cl^-$, was obtained in 90% yield.

$T_3Ge^+Cl^-$.—Addition of germanium tetrachloride (2.9 g., 0.013 mole) in 50 ml. of chloroform to tropolone (5.0 g., 0.039 mole) in 150 ml. of chloroform gave a white precipitate. The crude product analyzes approximately for $(C_7H_5O_2)_2GeCl_2$. *Anal.* Calcd. for $(C_7H_5O_2)_2GeCl_2$: C, 43.6; H, 2.59; Ge, 18.9; Cl, 18.5. Found: C, 45.5; H, 3.00; Ge, 17.9; Cl, 17.6. It is isomorphous with T_2SnCl_2 from X-ray powder pattern analyses. The crude

(14) R. G. Pearson, D. N. Edington, and F. Basolo, *J. Am. Chem. Soc.*, **84**, 3233 (1962).

(15) The details of the hydrolysis studies will be described in the next paper of this series.
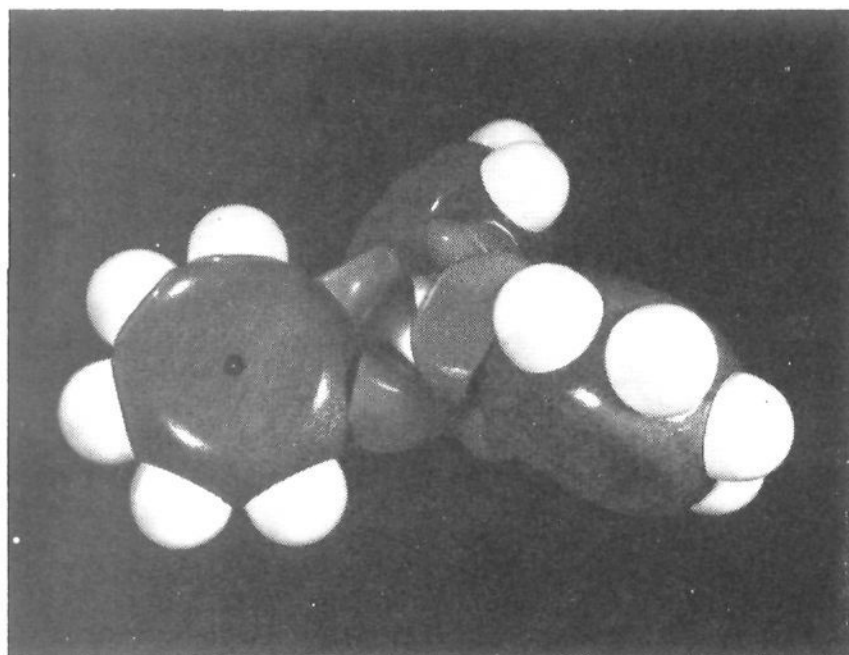
Fig. 1.—Model of the T_3Si^+ cation.
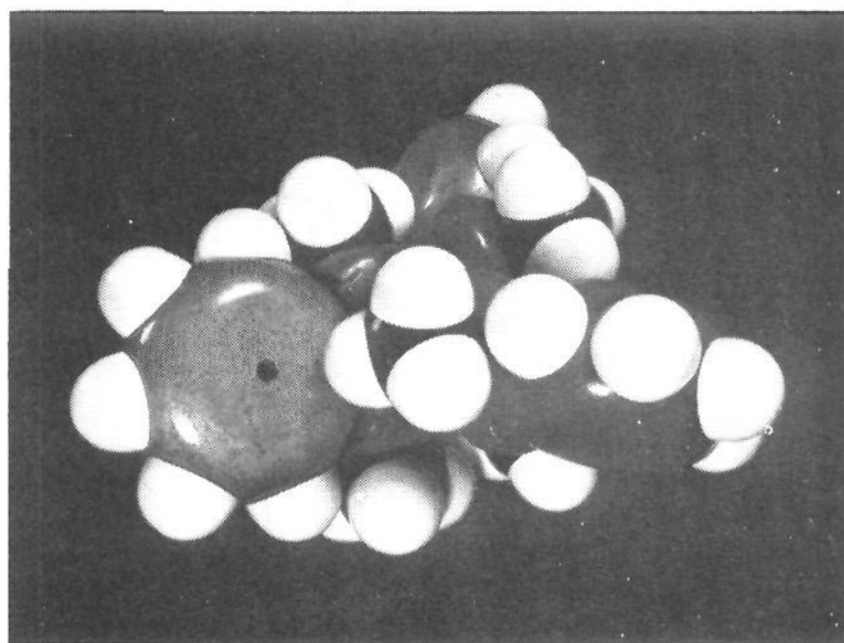
Fig. 2.—Model of the A_3Si^+ cation.

Fig. 3.—Model of the A_2B^+ cation.

bis chelate was converted to $T_3Ge^+Cl^-$ by recrystallization from a 50–50 water–methanol mixture and was obtained in 60% yield.

$T_3P^{2+}2I^-$.—Phosphorus pentachloride (8.4 g., 0.04 mole) was added to tropolone (14.7 g., 0.12 mole) in 250 ml. of chloroform. The reaction slurry was heated to reflux for 1 hr., and then filtered. The crude white solid was dissolved in 50 ml. of water and a solution of sodium iodide (6 g.) in 10 ml. of water was added to give the red solid, $T_3P^{2+}2I^-$, in 47% yield. Red crystals were obtained by recrystallization from a 50–50 water–methanol mixture.

Lithium Salt of N,N′-Dimethylaminotroponimine.—To a stirred solution of N,N′-dimethylaminotroponimine[16] (11.8 g. 0.08 mole) in 60 ml. of benzene at 0° was added gradually 52 ml. of a hexane solution of 15% n-butyllithium (0.08 mole) so that the temperature did not rise above 15°. The ice bath was removed after the addition and the mixture was stirred 15 min. The lithium salt precipitated as a yellow solid. This was used as an intermediate in the preparation of the following compounds.

$A_2B^+Br^-$.—A solution of boron tribromide (10 g., 0.04 mole) in 50 ml. of benzene was added to the slurry of the N,N′-dimethylaminotroponimine lithium salt (0.08 mole). A yellow solid separated during the addition. The mixture was then heated to reflux and swept with nitrogen for 2 hr. The solid was recrystallized from hot water with charcoal to give $A_2B^+Br^-$, brown crystals in 90% yield.

$A_3Si^+Cl^-$.—In a similar procedure, silicon tetrachloride (4.3 g., 0.025 mole) in 30 ml. of heptane was added dropwise to 0.096 mole of the lithium salt of the ligand. A yellow solid separated upon addition. The slurry was heated to reflux and swept with a rapid stream of nitrogen for 2 hr. The solid was isolated by filtration and converted to the iodide by the addition of a solution of sodium iodide (5 g.) in 10 ml. of water to the crude solid dissolved in 50 ml. of water. A red-brown precipitate appeared, which was dissolved in hot methanol, decolorized with charcoal, and cooled to give orange-red crystals of $A_3Si^+Br^-$ in a yield of 67% based on silicon tetrachloride.

$A_3Ge^+I^-$.—Addition of germanium tetrabromide (10.0 g., 0.025 mole) in 30 ml. of heptane to a slurry of 0.075 mole of the N,N′-dimethylaminotroponimine lithium salt gave a brown precipitate. After filtration, the solid was dissolved in a minimum amount of water, and a saturated aqueous solution of sodium iodide was added until no precipitate formed upon further addition. The brown precipitate was collected, dissolved in a hot 50–50 water–methanol mixture and decolorized with charcoal. Orange-brown crystals of $A_3Ge^+I^-$ were obtained in 40% yield after recrystallization from water.

$A_3Sn^+Br^-$.—Tin tetrabromide (12.3 g., 0.028 mole) in 60 ml. of hexane was added dropwise to a suspension of the lithium salt of the ligand (0.086 mole). A yellow precipitate appeared during the addition. Then, the mixture was refluxed and swept with nitrogen for 2 hr. The product was collected by filtration and recrystallized from methanol to give $A_3Sn^+Br^-$ in 80% yield.

Aqueous Preparation of Cationic Tropolone Chelates.—A solution of silicon tetrachloride (2 g., 0.01 mole) in 10 ml. of benzene was added to 80 ml. of a 50–50 mixture of water and methanol.
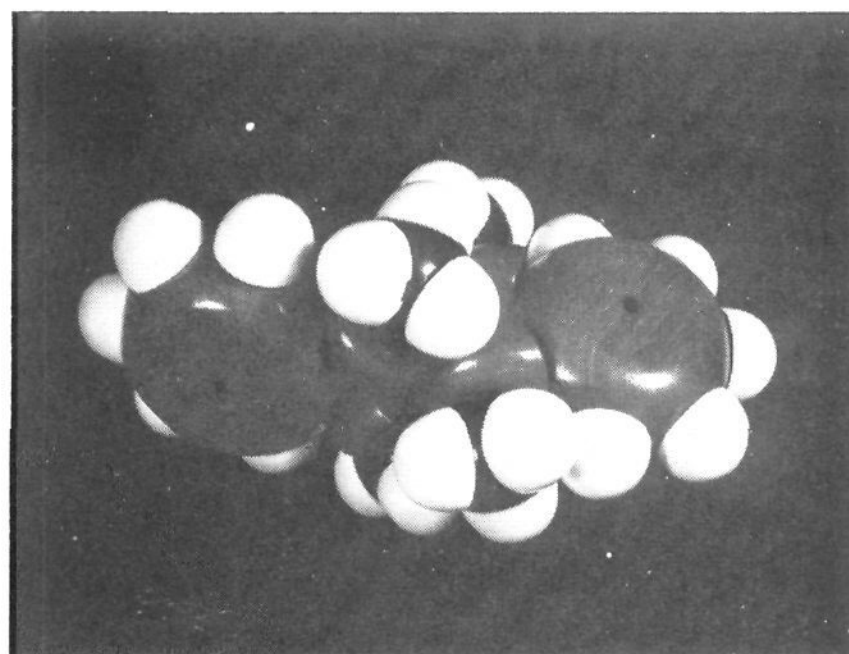
After stirring this mixture for several minutes, tropolone (5 g., 0.04 mole) was added, and the mixture was refluxed for 1 hr. The reaction mixture was filtered, and a concentrated solution of ammonium hexafluorophosphate was added to give a colorless precipitate which was recrystallized from a water–methanol mixture. This proved by comparison of the infrared spectra and melting points to be identical with $T_3Si^+PF_6^-$.

The above procedure was followed with substitution of germanium tetrachloride. The product was identical with an authentic sample of $T_3Ge^+PF_6^-$.

Boric acid (0.62 g., 0.01 mole) and tropolone (2.5 g., 0.02 mole) were added to 70 ml. of a 50–50 mixture of methanol and water which contained 3 ml. of concentrated hydrochloric acid. The reaction mixture was heated on a steam bath until all of the solids went into solution. A concentrated solution of ammonium hexafluorophosphate was added, and on cooling the solution yielded colorless needles which were identical with authentic $T_2B^+PF_6^-$. The yield was 60%.

Cationic Chelate Salts. General.—A number of chelate salts were prepared simply by metathetical reactions in aqueous media. Analytical data for all of these salts are given in Table I. All salts were recrystallized from either water, water–methanol, or water–acetonitrile. Recrystallization from chlorinated solvents may also be effected but often in these cases there is retention of solvent.

Many of the salts of the tropolone chelates are colored. The origin of the color in the solid state is probably a charge transfer from the anion to the chelate. Consistently, the color deepens through the halide series from chloride to iodide; e.g., $T_2B^+PF_6^-$ and $T_2B^+Cl^-$ are colorless, $T_2B^+Br^-$ is yellow, and $T_2B^+I^-$ is red.

The hexafluorophosphate salts of T_3Si^+ and T_3Ge^+ are isomorphous but the corresponding iodides are not.

The infrared spectra of the T and A chelates are dominated by ligand absorptions in the 4000- to 800-cm.$^{-1}$ region. The ligand absorptions show similarity within a given class of chelate, i.e., $chel_3M^+$, $chel_3M$, etc.

(16) R. Brasen, H. E. Holmquist, and R. E. Benson, J. Am. Chem. Soc., **82**, 995 (1960).

TABLE I
CATIONIC CHELATES OF TROPOLONE

Formula	M.p., dec., °C	Color	Calcd. C	Calcd. H	Calcd. X⁻	Calcd. M	Found C	Found H	Found X⁻	Found M
$T_2B^+Br^-$	278	Yellow	50.5	3.01	24.0	3.26	49.4	3.71	24.0	3.06
$T_2B^+I^-$	280–285	Red	44.3	2.64	33.4	2.86	44.3	2.92	32.6	2.98
$T_2B^+PF_6^-$	196–198	White	42.8	2.59	7.82^a	2.72	42.5	2.53	7.47^a	2.69
$T_2B^+Cr(SCN)_4(NH_3)_2$		Pink	37.3	9.10^b	22.2^c	1.87	38.1	8.88^b	22.6^c	2.22
$T_3Si^+Cl^-$	335–342	White	59.0	3.51	8.33	6.59	58.0	3.79	8.42	6.77
$T_3Si^+PF_6^-$	. . .	White	47.0	2.82	5.97^a	5.22	47.1	3.13	5.53^a	5.26
$T_3Ge^+Cl^-$	315–395	White	53.5	3.19	7.51	15.4	52.8	3.46	7.90	14.8
$T_3Ge^+PF_6^-$	325–330	White	43.4	2.58	5.33^a	12.5	43.4	3.09	5.22^a	11.0
$T_3P^{2+}2(PF_6)^-$	. . .	Colorless	36.9	2.21	33.4^d	13.6	36.9	2.19	32.9^d	13.0
$T_3P^{2+}2I^-$	250	Red	38.9	2.31	39.2	4.78	38.5	3.09	37.3	4.90

^{a} Phosphorus. ^{b} Chromium. ^{c} Sulfur. ^{d} Fluorine.

TABLE II
CATIONIC CHELATES OF N,N'-DIMETHYLAMINOTROPONIMINE

Salt	M.p., °C	Color	Calcd. C	Calcd. H	Calcd. N	Calcd. X⁻(P)	Calcd. M	Found C	Found H	Found N	Found X⁻(P)	Found M
$A_2B^+Br^-$	295–296 dec.	Brown	56.1	5.67	14.6	20.8	2.81	55.2	6.21	14.4	21.0	2.76
$A_2B^+PF_6^-$	151–160 dec.	Yellow	48.0	4.92	12.5	(6.90)	2.41	48.7	5.43	12.4	(6.87)	2.67
$A_3Si^+PF_6^-$	269 dec.	Yellow	52.6	5.39		(5.06)	4.57	52.7	5.06		(5.37)	4.87
$A_3Ge^+PF_6^-$	295 dec.	Yellow	49.2	5.01		(4.72)	11.0	48.1	4.97		(4.98)	10.9
$A_3Ge^+I^-$	346–348 dec.	Orange-brown	50.5	5.14	13.1	19.8	11.3	49.1	5.65	13.8	18.7	10.2
$A_3Sn^+Br^-$	277–278	Yellow	50.6	5.16	13.2	12.5	18.6	49.8	5.45	12.4	13.0	18.4
$A_3Sn^+I^-$	282–283	Yellow	47.2	4.84	12.2	18.5	17.3	46.2	5.00	11.9	17.9	17.0

Reaction of $A_2B^+Br^-$ and $LiAlH_4$.—The chelate, $A_2B^+Br^-$, (10 g., 0.026 mole) was added slowly to a slurry of lithium aluminum hydride (1.1 g., 0.029 mole) in 700 ml. of glyme which had been refluxing approximately 12 hr. The solution turned deep red, and gas was evolved. The mixture was then filtered under nitrogen. The red filtrate was evaporated to dryness under reduced pressure. The dark red solid was extracted with toluene which was then evaporated under reduced pressure. The red solid was recrystallized from n-hexane (m.p. 100° dec., ~155° melts). Anal. Calcd. for $(C_9H_{11}N_2)B-(C_9H_{12}N_2)$: C, 70.7; H, 7.55; N, 18.4; B, 3.5. Found: C, 71.4; H, 7.9; N, 18.6; B, 3.5. The proton n.m.r. spectrum at 60 Mc. in deuterated benzene showed two methyl proton resonances at −104 and −108 c.p.s., an aliphatic proton resonance (triplet) at −144 c.p.s., and aromatic proton resonances at −323 to −393 c.p.s. (tetramethylsilane reference).

Preparation of Group III M T_3 Chelates.—To a solution of tropolone (10 g., 0.0828 mole) in 250 ml. of methanol was added a solution of aluminum chloride (3 g., 0.0147 mole) in 100 ml. of methanol. A precipitate formed immediately. The slurry was heated to reflux and filtered. The insoluble solid (4.75 g., 83% yield) was recrystallized from a hot acetonitrile–methanol mixture, m.p. >360°. Anal. Calcd. for $Al(O_2C_7H_5)_3$: C, 64.7; H, 3.86; Al, 7.1. Found: C, 63.6; H, 3.91; Al, 6.4.

The gallium and indium chelates were prepared by adding a solution of $GaBr_3$ or $InCl_3$ (0.02 mole) in 50 ml. of methanol and 10 ml. of water to a solution of tropolone (0.06 mole) in 200 ml. of methanol and 25 ml. of water. There was an immediate precipitate. The slurry was heated to reflux for 1 hr. and then cooled. The solid was recovered by filtration (crude yields were about 80–90%). The gallium derivative was recrystallized from hot chloroform (m.p. >400°) and the indium from a hot water–methanol–acetonitrile mixture (m.p. 369–372°). Anal. Calcd. for $Ga(O_2C_7H_5)_3$: C, 59.3; H, 3.40; Ga, 16.1; mol. wt., 433. Found: C, 58.2; H, 3.67; Ga, 15.7; mol. wt., 499. Calcd. for $In(O_2C_7H_5)_3$: C, 52.8; H, 3.18; In, 24.0. Found: C, 52.0; H, 3.35; In, 23.3.

Thallium chloride (0.02 mole) was suspended in 200 ml. of water, and chlorine was bubbled into the solution until all the thallium chloride dissolved. Nitrogen was then rapidly passed through the solution to remove excess chlorine. The resultant solution was added to a solution of tropolone (0.065 mole) in 150 ml. of methanol and 50 ml. of water. A yellow solid separated during the addition. It was recovered by filtration and then recrystallized from hot toluene, m.p. 184–185°. Anal. Calcd. for $Tl(O_2C_7H_5)_3$: C, 44.4; H, 2.66. Found: C, 44.6; H, 2.85.

Preparation of Rare Earth Chelates.—Tropolone (0.045 mole) in a mixture of 100 ml. of methanol and 50 ml. of water was added to a solution of 0.01 mole of $LaCl_3 \cdot 7H_2O$ in a mixture of 50 ml. of water and 25 ml. of methanol. Four drops of ammonium hydroxide was added and the solution was heated to 70° for a period of 45 min. during which time a solid separated. The solid was collected, washed, and dried. Anal. Calcd. for $La(C_7H_5-O_2)_3$: La, 27.6; C, 50.3; H, 3.02. Found: La, 26.3; C, 49.7; H, 3.26. A similar procedure was followed with europium trichloride. Anal. Calcd. for $Eu(C_7H_5O_2)_3$: Eu, 29.0; C, 48.8; H, 2.95. Found: Eu, 28.8; C, 48.9; H, 3.16.

Preparation of $NaInT_4$.—Indium trichloride (2.2 g., 0.01 mole) was dissolved in a minimum of methanol and then added slowly to a solution of tropolone (6.1 g., 0.05 mole) in 200 ml. of water and 20 ml. of methanol which contained 0.1 mole of sodium hydroxide. The resultant slurry was heated to reflux for 1 hr. and filtered while hot. Anal. Calcd. for $NaIn(O_2C_7H_5)_4$: Na, 3.7; In, 18.5; C, 54.0; H, 3.22. Found: Na, 4.2; In, 18.7; C, 52.3; H, 3.31.

Reaction of $SbCl_5$ and Tropolone.—A solution of antimony pentachloride (0.03 mole) in 80 ml. of chloroform was added to a solution of tropolone (0.12 mole) in 150 ml. of chloroform. During the addition, the solution turned yellow, and then a yellow solid separated. The slurry was heated to reflux for 30 min., cooled to 25°, and filtered. The insoluble material (3.72 g.) was set aside. The filtrate was concentrated by vacuum evaporation and then filtered to yield 6.4 g. of a yellow solid which was recrystallized from hot chloroform, m.p. 208° (56% yield). Anal. Calcd. for $SbCl_4(O_2C_7H_5)$: Sb, 31.8; Cl, 36.8; C, 21.7; H, 1.31. Found: Sb, 31.6; Cl, 37.2; C, 21.4; H, 1.69.

Reaction of Tropolone and As_2O_5.—A mixture of As_4O_{10} (0.0025 mole) and tropolone (0.03 mole) in 35 ml. of ethanol, 35 ml. of water, and 7 ml. of concentrated hydrochloric acid was heated to ~75° for 1.5 hr. Almost all of the As_2O_5 dissolved within 15 min. The solution was filtered while hot, and about one-half the solvent was removed under reduced pressure to give a slurry. The slurry was filtered to give 3.9 g. of a white solid, which was recrystallized from a hot methanol–water mixture, m.p. 252–252.5°. Anal. Calcd. for $ClAs(OH)_2(O_2C_7H_5)_2 \cdot H_2O$: Cl, 8.8; As, 18.5; C, 41.6. Found: Cl, 8.8; As, 18.4; C, 41.4. The above procedure was repeated with substitution of 48% hydrobromic acid for the hydrochloric acid. The crude product weighed 3.05 g. (theory 4.3), and was recrystallized from a water–methanol mixture, m.p. 201–203.5°. Anal. Calcd. for $(C_7H_5O_2)_2As(OH)_2^+-Br^-$: As, 17.6; Br, 18.5. Found: As, 17.6; Br, 17.7.

The chloride, $ClAs(OH)_2(O_2C_7H_5)_2 \cdot H_2O$, was dissolved in water–methanol and a concentrated solution of NH_4PF_6 was added. A precipitate slowly formed. This was collected and recrystallized from hot water–ethanol. This material showed the infrared PF stretching frequency characteristic of PF_6^-.

Analysis was in only fair agreement for $As(OH)_2(O_2C_7H_5)_2PF_6$. *Anal.* Calcd. for $As(OH)_2(O_2C_7H_5)_2PF_6$: C, 33.8; F, 22.9; Cl, 0.00. Found: C, 32.2; F, 20.6; Cl, <0.05. Addition of salts of other large anions, *e.g.*, I^- and $B_{10}H_{10}{}^{2-}$, to solutions of $ClAs(OH)_2(O_2C_7H_5)_2 \cdot H_2O$ gave precipitates, but these on recrystallization analyzed only approximately for the appropriate $XAs(OH)_2(O_2C_7H_5)_2$ species owing to partial hydrolysis.

Preparation of T_2SbCl.—Antimony trichloride (2.3 g., 0.01 mole) was dissolved in 5 ml. of concentrated hydrochloric acid and 15 ml. of methanol. This was added to a solution of tropolone (4.3 g., 0.035 mole) in 60 ml. of methanol, 20 ml. of water, and 1 ml. of concentrated hydrochloric acid. The solution was heated to reflux and solid began to slowly separate. The reaction mixture was held at reflux for 15 min. and then cooled. The crude solid was collected and weighed 3.9 g. (theory, 4.0 g.). It was recrystallized from hot methanol to give yellow crystals, m.p. 273–278° dec. *Anal.* Calcd. for $(C_7H_5O_2)_2SbCl$: Sb, 30.5; Cl, 8.88. Found: Sb, 30.3; Cl, 8.70. This compound was not soluble in most common solvents. The cryoscopic molecular weight was determined in dimethyl sulfoxide; theory, 399.3; found, 364.

Preparation of T_2BiCl.—Bismuth nitrate (4.9 g., 0.01 mole) was dissolved in 15 ml. of concentrated hydrochloric acid and 20 ml. of methanol. This was added to a solution of tropolone (4.3 g., 0.035 mole) in 80 ml. of methanol and 2 ml. of concentrated hydrochloric acid. The solution was heated, and water was added until a state of incipient precipitation was obtained. Reflux conditions were maintained for 30 min. On cooling, cream-colored crystals separated. These were recrystallized from methanol, m.p. 311–313° dec. *Anal.* Calcd. for $(C_7H_5O_2)_2BiCl$: C, 34.5; H, 2.06; Bi, 43.0; Cl, 7.30. Found: C, 34.4; H, 2.18; Bi, 42.5; Cl, 7.23.

Preparation of T_2SnCl_2.—A solution of tin tetrachloride (6.2 g., 0.023 mole) in 100 ml. of chlorobenzene was added to a solution of tropolone (12 g., 0.098 mole) in 150 ml. of chlorobenzene. On addition of the tin tetrachloride a white precipitate formed. The slurry was heated to 80° for 2 hr. and then filtered. The solid was thoroughly washed with diethyl ether. The weight of the crude product was 10 g. (theory, 10.2 g.), m.p. 365–370° dec. *Anal.* Calcd. for $SnCl_2(O_2C_7H_5)_2$: Sn, 27.5; C, 38.9; H, 2.34. Found: Sn, 27.3; C, 39.5; H, 2.71. A product identical with the above by infrared and melting point comparison was obtained from the reaction of tin tetrachloride pentahydrate and tropolone in a water–methanol mixture.

Single crystal X-ray data for T_2SnCl_2 were analyzed by Dr. John Whitney. The crystals are of the orthorhombic system. Cell dimensions are $a = 14.63$, $b = 28.43$, and $c = 7.18$ Å. With eight molecules per unit cell and a measured density of 1.92 g./cc., the calculated molecular weight of T_2SnCl_2 is 433 ± 3 (theory 431.6).

Preparation of T_2SnBr_2.—A solution of tin tetrabromide (12 g., 0.027 mole) in 100 ml. of toluene was added to a solution of tropolone (12 g., 0.098 mole) in 200 ml. of toluene. A copious cream solid separated. After the addition was complete, 150 ml. of dimethoxyethane was added, and the slurry was heated to reflux. Acetonitrile was added until everything was in solution at reflux. The hot solution was filtered and then concentrated by vacuum evaporation to give a yellow solid which was recrystallized from acetonitrile. *Anal.* Calcd. for $(C_7H_5O_2)_2SnBr_2$: C, 32.2; H, 1.92; Sn, 22.8; Br, 30.7. Found: C, 32.0; H, 2.03; Sn, 21.2; Br, 30.9.

Preparation of T_3SnCl.—A slurry of T_2SnCl_2 (4 g., 9 mmoles) and the silver salt of tropolone (2.1 g., 9 mmoles) in 200 ml. of dimethoxyethane and 250 ml. of acetonitrile was refluxed for 1 hr. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The crude solid residue was recrystallized from acetonitrile to give nearly colorless crystals, m.p. 298–305° dec. *Anal.* Calcd. for $SnCl(O_2C_7H_5)_3 \cdot CH_3CN$: Sn, 21.2; C, 49.4; H, 3.23; Cl, 6.36. Found: Sn, 21.2; C, 49.9; H, 3.37; Cl, 6.31. The infrared spectrum of this compound had a CN stretching frequency characteristic of the solvent acetonitrile.

A solution of tin tetrachloride (2.6 g., 0.01 mole) in 100 ml. of methanol was added to a slurry of the sodium salt of tropolone (4.3 g., 0.03 mole) in 100 ml. of methanol. The mixture was heated to reflux, and then 200 ml. of acetonitrile was added. The slurry was stirred and held at a mild reflux for 4 hr. An additional 200 ml. of acetonitrile was added to the refluxing mixture. The reaction mixture was filtered while hot, and the crude solid was recrystallized from acetonitrile to give nearly colorless crystals, m.p. 312–317°. *Anal.* Calcd. for $SnCl(C_7H_5O_2)_3 \cdot$

CH_3CN: Cl, 6.36; C, 49.4; H, 3.23. Found: Cl, 6.31; C, 49.3; H, 3.27. Dr. John Whitney established from single X-ray crystal data that the crystals belong to the monoclinic system with the cell dimensions of $a = 9.30$, $b = 23.8$, $c = 10.27$ Å., and $\beta = 100°$ and the space group, $P2_{1/c}$. There are four molecules per unit cell. The molecular weight for this compound was calculated to be 552.1 (theory 558.2) from the experimental density of 1.622 g./cc.

Preparation of $C_6H_5SnT_3$.—A solution of $C_6H_5SnCl_3$ (0.02 mole) in 30 ml. of benzene was added to a solution of tropolone (0.07 mole) in 100 ml. of ether. A yellow gum separated. Dimethoxyethane (100 ml.) was added and the reaction mixture was heated on a steam bath for 2 hr. The solid product was collected (9.1 g.) and recrystallized from acetonitrile, m.p. 248–252°. *Anal.* Calcd. for $C_6H_5SnClT_2$: C, 50.7; H, 3.26; Sn, 25.0; Cl, 7.5. Found: C, 49.5; H, 3.33; Sn, 24.9; Cl, 6.9.

A mixture of $C_6H_5SnClT_2$ (0.01 mole), sodium tropolonate (0.012 mole), and acetonitrile (250 ml.) was heated to reflux for 1 hr. Then 40 ml. of water and 20 ml. of methanol were added, and reflux was maintained for 15 min. The hot slurry was filtered and the solid was recrystallized from acetonitrile, m.p. 298–302°. *Anal.* Calcd. for $C_6H_5SnT_3$: C, 58.1; H, 3.98; mol. wt., 558.7. Found: C, 57.8; H, 3.92; mol. wt. (CH_2Cl_2), 545. Recrystallization from dichloromethane yielded a solvate of $C_6H_5SnT_3$. *Anal.* Calcd. for $C_6H_5SnT_3 \cdot 1.5CH_2Cl_2$: C, 50.0; H, 3.39; Sn, 17.3; Cl, 15.6. Found: C, 50.0; H, 3.49; Sn, 16.9; Cl, 15.2.

Preparation of GeT_4.—Addition of silver tropolonate (1.5 g., 0.0065 mole) dissolved in 120 ml. of 75% acetonitrile–water solution to $T_3Ge^+Cl^-$ (3.0 g., 0.0065 mole) in 50 ml. of 75% acetonitrile–water gave a white-gray solid. The solid was isolated by filtration and identified as AgCl. The yellow-orange filtrate was concentrated to 30 ml. under reduced pressure during which time a yellow-orange sludge formed. Filtration isolated a yellow-orange solid, which was red after air drying and black after vacuum drying. Recrystallization from 99:1 acetonitrile–water gave red crystals, which turned black when vacuum dried. *Anal.* Calcd. for $(C_7H_5O_2)_4Ge$: C, 60.3; H, 3.61; Ge, 13.05. Found: C, 59.3; H, 3.84; Ge, 12.9. On exposure to moist air, the crystals absorbed 2 equiv. of water and became red (m.p. 115–116°). *Anal.* Calcd. for $(C_7H_5O_2)_4Ge \cdot 2H_2O$: C, 56.8; H, 4.05; Ge, 12.5. Found: C, 56.1; H, 4.29; Ge, 12.3.

Preparation of SiT_4.—Silver tropolonate (3.0 g., 0.013 mole) dissolved in 200 ml. of acetonitrile and 60 ml. of water was added to $T_3Si^+Cl^-$ (5.5 g., 0.013 mole) in 80 ml. of acetonitrile and 24 ml. of water. A white-gray precipitate of silver chloride separated. The filtrate was concentrated to 30 ml. and the yellow-orange sludge was isolated by filtration. Recrystallization from 99% acetonitrile–1% water solution gave red crystals, m.p. 120–125°. *Anal.* Calcd. for $(C_7H_5O_2)_4Si \cdot 2H_2O$: C, 61.4; H, 4.38; Si, 5.12. Found: C, 61.2; H, 4.37; Si, 5.33. On vacuum drying for 4 hr. at 80°, the red crystals became black. *Anal.* Calcd. for $(C_7H_5O_2)_4Si$: C, 65.6; H, 3.90; Si, 5.47. Found: C, 65.2; H, 4.32; Si, 5.82.

Preparation of SnT_4.—A solution of tin tetrachloride (2.6 g., 0.01 mole) in 150 ml. of acetonitrile warmed to 60° was added to a slurry of the sodium salt of tropolone (5.8 g., 0.04 mole) in 400 ml. of acetonitrile. The slurry was stirred and heated to reflux, and then water was added until all solids went into solution. The solution was filtered and then reduced to approximately one-half its volume under reduced pressure. The slurry was filtered to give a pale yellow solid which was recrystallized from a water–acetonitrile mixture, m.p. 357–358° dec. *Anal.* Calcd. for $Sn(O_2C_7H_5)_4$: Sn, 19.7; C, 55.8; H, 3.32. Found: Sn, 19.7; C, 54.2; H, 3.60. The infrared spectrum of this compound in the region from 4000 to 800 cm.$^{-1}$ was essentially identical with that of PbT_4 and ZrT_4. This procedure tends to give T_3SnOH as a major product. An alternative synthesis will be reported in paper III of this series.

Preparation of PbT_4.—A slurry of lead tetraacetate (3 g., 0.0068 mole) and 100 ml. of benzene was added to a solution of tropolone (7 g., 0.057 mole) in 150 ml. of benzene. There was an immediate orange-brown coloration, and a solid separated. The slurry was stirred for 1 hr. and then filtered. The crude solid weighed 3.8 g. (theory 4.7 g.) and was recrystallized from dichloromethane, m.p. 99° dec. *Anal.* Calcd. for $Pb(O_2C_7H_5)_4$: Pb, 30.0; C, 48.7; H, 2.92. Found: Pb, 31.3; C, 48.2; H, 3.01.